

Structural and thermodynamic properties of heavily mechanically deformed Ru and AlRu

E. Hellstern, H. J. Fecht, Z. Fu, and W. L. Johnson

W. M. Keck Laboratory of Engineering Materials, California Institute of Technology, Pasadena, California 91125

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We report on high-energy ball milling of Ru and AlRu. The deformation results in a drastic decrease of the crystal size to a nanometer scale and in an increase of atomic-level strain. This is accompanied by a disordering of the crystal lattice as is shown by means of the long-range-order parameter in AlRu. The specific heat increases by more than 15%–20%, indicating large changes in the vibrational and configurational part of the entropy. The stored energy of cold work is up to 6 kJ/mol for AlRu and 10 kJ/mol for Ru. This is almost 40% of the heat of fusion of Ru and exceeds by far the energies stored by other deformation processes.

I. INTRODUCTION

Investigations on mechanical deformation of pure elements and intermetallic phases have always been of prime interest in materials research because of their immediate impact on industrial application. The various types of defects introduced by cold work and their interactions have been studied extensively, and it has been shown that elastic and plastic deformation changes the thermodynamic functions of metals.¹ However, the stored energy of cold work rarely exceeds 5% of the heat of fusion of the metal, even after severe mechanical deformation.

Intensive deformation under nonisothermal conditions especially occurs in high-energy ball milling of metal powder. Recently, it has been shown that this process can even result in glass formation from elemental powder mixtures or intermetallic compound powders.^{2,3} When amorphization is achieved by mechanically alloying the pure elements, the deformation energies are small compared to the large negative heat of mixing, which provides the driving force for a solid-state amorphizing reaction.^{4,5} In contrast, ball milling of the intermetallic compound starts with a chemically homogeneous material. For a crystal-to-glass transition to proceed, the free energy of the crystal has to be raised above the free energy of the amorphous phase.⁶ Up to now, it is still an open question as to how the crystal is destabilized by mechanical deformation. Since the transformation requires energies which are comparable to the heat of fusion of the metal, effective mechanisms for the storage of deformation energies are required.

To get more insight into this problem, we investigated both a pure element and an intermetallic compound after different stages of ball milling. Ru has been chosen because its high melting temperature implies a high temperature for recovery and recrystallization. Therefore, Ru should be capable of storing large deformation energies. In addition, elemental Ru is relatively stable against oxidation, which diminishes the influence of oxygen contamination. As the intermetallic compound we chose AlRu, which has the CsCl structure. Information on how long-range order is affected in a mechanically destabilized crystal is obtained by means of the long-range-order parameter S . This parameter can be

determined experimentally by investigating the superlattice lines of the ordered solution by x-ray diffraction. The intensity of these superlattice lines depends on the difference of the atomic scattering factors of the constituent elements. This in turn is proportional to the difference in atomic number. In the case of a completely ordered AlRu crystal, the superlattice reflections should have about 30% of the intensity of the fundamental lines. In addition, this compound is rather refractory, with a melting point of 2000 °C. This, as in the case of Ru, results in low recovery of stored defects at ambient temperature. Together, these factors make the compound ideally suited for this study.

II. EXPERIMENTAL DETAILS

Elemental Ru with a purity of 99.95% and a particle size of ~ 120 mesh was used in the experiment. For the preparation of the AlRu compound, Ru and Al powders (99.995% purity) were carefully mixed, pressed into a pellet, sealed in a quartz tube, and annealed at 1000 °C for 3 days. After cooling to room temperature, the pellet was ground to a fine powder. The ball milling was done in a shaker mill (Spex 8000) with hardened steel balls and vial. The powder was sealed in the steel container and opened after different ball-milling times to take out a small amount of powder. All the handling was done in a glove bag under an argon atmosphere. Chemical analysis of the Ru powder was done by an energy-dispersive x-ray detector (EDAX 9900). It showed considerable iron impurities due to wear debris after long milling time (3%, 5%, and 10% Fe after 8-, 16-, and 32-h ball milling, respectively). In the case of AlRu, the Fe content was much less (1%, 3%, and 5% after 16, 32, and 64 h). Since Fe is isoelectronic with Ru and forms an isotypic "CsCl" compound, we expect the Fe impurities to form solutions with relatively small excess heat of mixings.

The x-ray diffractograms were taken with a Norelco diffractometer in step-scanning mode using $\text{CuK}\alpha$ radiation ($\lambda = 0.1542$ nm) filtered with a nickel foil. The transmission electron microscopy was done with a Phillips EM 430. The powder was mixed with epoxy, and thin slices of about 20–50-nm thickness were cut with a microtome using a diamond knife.

The thermal analysis of the powder was made with a differential scanning calorimeter (DSC) (Perkin-Elmer DSC4) connected with an Apple II computer for data processing. The heating was done in a sealed Al pan with a heating rate of 20 K/min under a flow of purified argon. After each DSC scan, a subsequent second scan was carried out without changing the sample configuration and used as reference. For the investigation of the stored enthalpy, the typical sample mass was 40 mg. A considerably larger mass of up to 300 mg was used for the specific heat experiments. The DSC4 was cooled to liquid-nitrogen temperature. The investigated temperature range was divided in smaller intervals of about 80 K. Starting from the lowest temperature, three subsequent scans were made for each interval before going to a higher temperature. Scans of the empty Al pan, of a sapphire single crystal (which was used as standard), and of the sample were used for the calculation of the specific heat. Small changes of the baseline, which can occur when the experiment is performed over a large temperature interval, are avoided by this technique. Thus, the relative error of the experiment is less than 3%.

III. RESULTS

Figures 1(a) and 1(b) show x-ray diffraction patterns before and after 32 h of ball milling. The x-ray scans show the characteristic diffraction lines of the hexagonal Ru and the cubic AlRu structure. In the case of AlRu, the superlattice reflections of the CsCl-type lattice are very strong. No additional x-ray lines are visible, which is an indication that Ru and AlRu form a solid solution with the Fe impurities after long ball milling. The initially sharp crystalline diffraction peaks are considerably broadened after ball milling as a result of the refinement of the microcrystallite size and an increase in internal strain. To separate these two effects, we plotted the full widths at half maximum of the Bragg peaks ΔK as a function of their K values. Each x-ray scan was corrected for $K\alpha$ and instrumental broadening. The line broadening owing to small crystal size is constant in K space and is given by⁷

$$\Delta K = 0.9(2\pi/d),$$

where d is the crystal size. The strain broadening is given by

$$\Delta k = A \langle e^2 \rangle^{1/2} K,$$

where A is a constant that depends on the strain distribution and is approximately one for a random distribution of dislocations. $\langle e^2 \rangle^{1/2}$ is the rms strain.⁸

Figure 2 shows the microcrystallite size d as a function of processing time. In the very beginning the ball milling leads to a fast decrease of the crystal size to less than 20 nm. Further refinement occurs slowly to 13 nm for Ru and 7 nm for AlRu after 32 or 64 h, respectively.

Direct observation of the individual Ru and AlRu particles was made by transmission electron microscopy (TEM). Figures 3(a) and 3(b) show high-resolution bright-field images of Ru and AlRu after 32 and 64 h. The crystallite size as estimated from the TEM pictures ranges from 11 to 14 nm for Ru and from 5 to 7 nm for AlRu, being in good agreement with the crystal size obtained from the broadening of

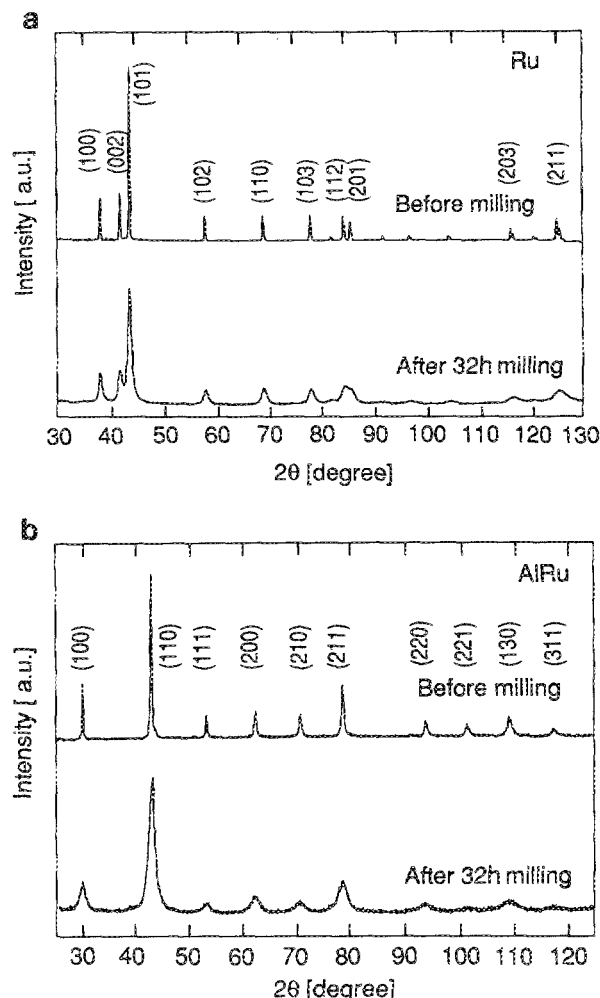


FIG. 1. X-ray diffraction patterns of (a) Ru and (b) AlRu before and after 32-h ball milling.

the x-ray diffraction peaks. The distribution of particle sizes is relatively narrow, which indicates that extended ball milling produces a uniform comminution. The corresponding diffraction patterns [see insets in Figs. 3(a) and 3(b)] and the lattice fringes of the crystals both show that the orientation of neighboring crystals is completely random. The individual crystals are separated by high-angle grain boundaries.

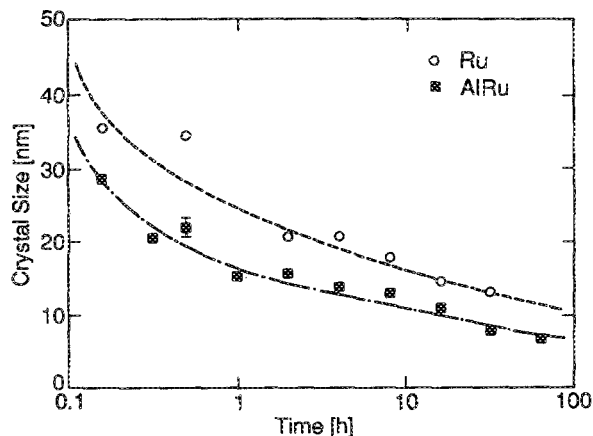


FIG. 2. Crystal size of Ru and AlRu as a function of ball-milling time.

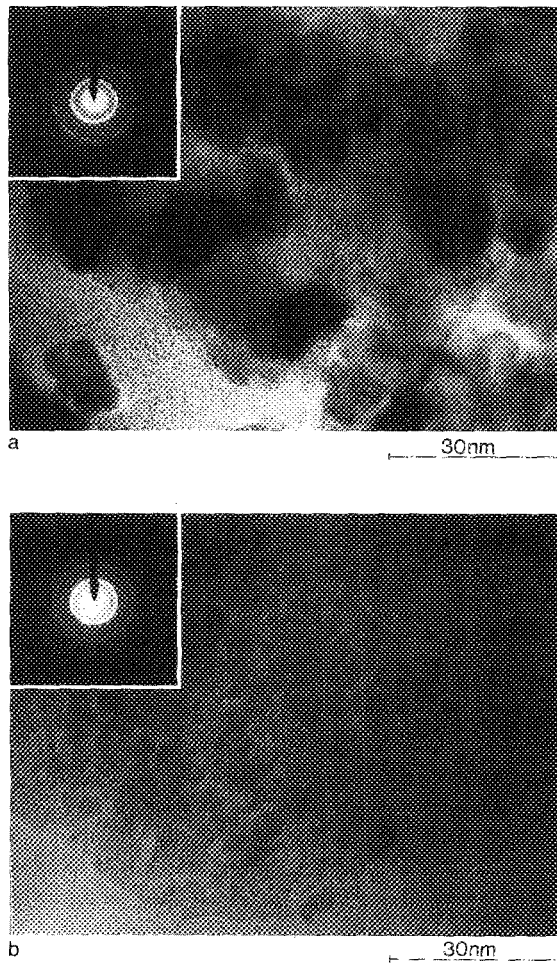


FIG. 3. TEM bright-field image of (a) Ru and (b) AlRu after 32- and 64-h milling, respectively. The insets show the corresponding diffraction patterns.

Because of the small crystallite size, the grain boundaries should contribute considerably to the physical properties of the metal. To come to a better understanding of the grain boundary contribution, we determined the strain, long-range-order parameter, stored energy, and specific heat versus reciprocal crystallite size. This is reasonable, since the ratio of atoms close to grain boundaries to those within the crystal is proportional to $1/d$. On the other hand, the milling time provides only an arbitrary scale for the evaluation of the material properties, since it depends strongly on the milling equipment, i.e., milling intensity, number of balls, size of the milling container, etc.

The rms strain as calculated from the x-ray broadening is shown in Fig. 4 as a function of reciprocal crystal size. The deformation leads to a strong increase in atomic-level strains. It reaches a maximum value of 1% for Ru and approximately 3% for AlRu. This maximum value is given at a crystal size of about 11–13 nm. For smaller crystals the rms strain remains constant for Ru or even decreases drastically for AlRu.

For the intermetallic compound AlRu, the long-range-order parameter S was determined by means of the intensities of the superlattice and fundamental x-ray lines of the CsCl structure.⁹ Whereas for the fundamental lines,

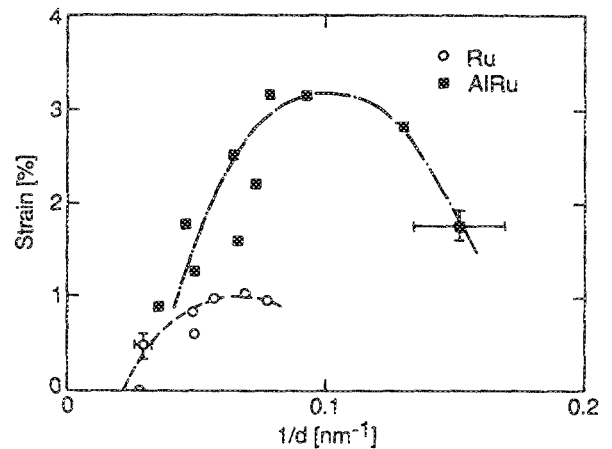


FIG. 4. Strain in Ru and AlRu as a function of reciprocal crystal size.

($h + k + l$) is even, the superlattice reflections are those for which ($h + k + l$) is odd (h, k , and l are Miller indices). The intensity of ten diffraction lines i.e., five fundamental and five superlattice reflections [see Fig. 1(b)], was used for the calculation of S by the equation

$$\frac{S}{S_0} = \left(\frac{(I^s/I_0^s)}{(I^f/I_0^f)} \right)^{1/2}$$

I^s , and I^f are the intensities of the superlattice or fundamental lines after ball milling compared to the intensity of the same lines I_0^s and I_0^f before ball milling. S_0 is the value for the unmilled sample. Figure 5 shows S/S_0 as a function of reciprocal crystal size. S/S_0 decreases rapidly to approximately 0.7, then changes only slightly with further decreasing crystal size. The dotted line shows the influence of the grain boundaries and will be discussed later.

In Fig. 6, DSC scans are shown for Ru and AlRu after 16-h ball milling. A broad exothermic reaction occurs for both samples. It begins at a temperature of ~ 370 K and is almost completed at 870 K. X-ray diffraction of the samples after the DSC runs shows that the heat release is mainly due to recovery and recrystallization. For Ru the size of the microcrystals is 22 nm and the strain is less than 0.4%. The

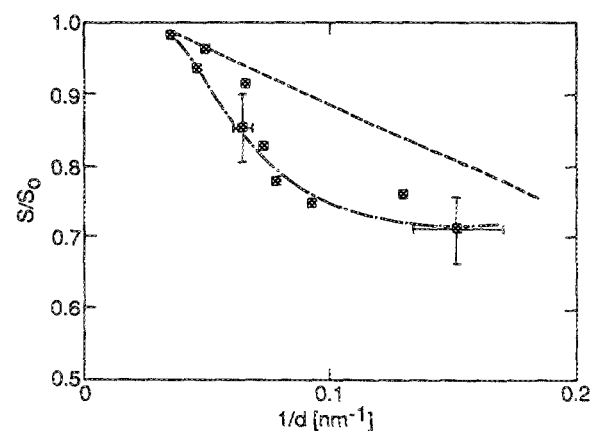


FIG. 5. Long-range-order parameter S of AlRu as a function of reciprocal crystal size. The dotted line was calculated assuming only disordering by grain boundaries.

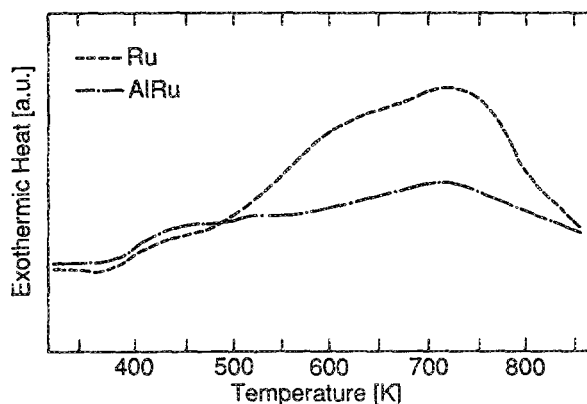


FIG. 6. DSC scans at 20 K/min for Ru and AlRu after 16-h milling.

residual stress after annealing at 870 K indicates that recovery is not entirely complete at 870 K. But additional differential thermal analysis (Perkin-Elmer DTA 1700) to 1670 K indicated that the heat release above 870 K is small. Therefore, the given values for the stored enthalpy as presented in Fig. 7 as a function of reciprocal particle size underestimate the true values only slightly. The stored enthalpy increases to a maximum value of ~ 10 kJ/mol for Ru and ~ 7 kJ/mol for AlRu. Further refinement results in a decrease of the heat release for both the Ru and AlRu system. The heat of mixing of Fe in Ru or AlRu should not contribute to the measured enthalpy release, since x-ray and TEM analysis show that Fe forms a solid solution already after ball milling.

Large differences also arise in the specific heat c_p at constant pressure. Figure 8 shows c_p of Ru before and after 32-h ball milling versus temperature. In the unmilled state the specific heat data agree well with previously published data taken from Ref. 10. After 32-h milling the specific heat increases 15%–20%. The specific heat increase Δc_p of Ru and AlRu at a constant temperature of 210 K is shown in Fig. 9 as a function of reciprocal particle size. Δc_p increases almost linearly with $1/d$. Annealing the Ru and AlRu samples with the smallest crystal size, i.e., the largest increase in Δc_p , for 3 days at 1370 K resulted in a partial decrease of Δc_p

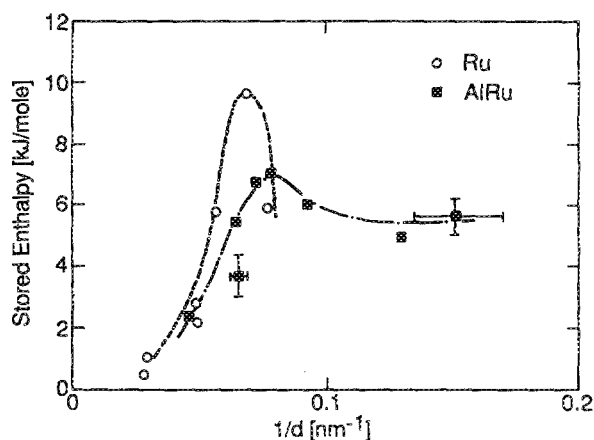


FIG. 7. Heat release for Ru and AlRu as a function of reciprocal crystal size.

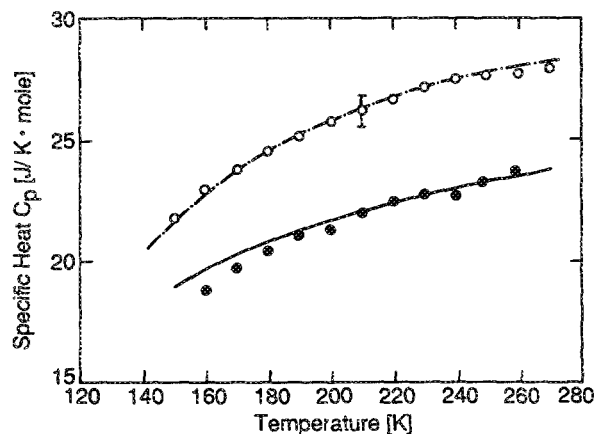


FIG. 8. Specific heat for Ru before and after 32-h milling as a function of temperature. The solid line shows data taken from Ref. 10.

from 20% to 7% for Ru and from 15% to 5% for AlRu. This establishes that a significant portion of the observed Δc_p is in fact associated with the particle-size comminution and lattice disorder produced by the ball milling.

IV. DISCUSSION

We observe that ball milling of Ru and AlRu decreases the crystal size and increases the lattice strain. Although after long processing time the crystal dimensions are in the order of 7–15 nm, further refinement seems to be difficult to achieve. This can be understood by considering the mechanisms for crystal refinement. Plastic deformation occurs by the glide of dislocations when a critical shear stress is applied. A lower-yield stress σ_y is required to maintain plastic deformation in a polycrystalline material. The Hall-Petch relationship describes the dependence of σ_y on the grain size of the material: $\sigma_y = \sigma_0 + kd^{-1/2}$, where σ_0 and k are constants, and d is the average grain diameter.¹¹ An extrapolation of this relation to nanocrystalline dimensions shows that very high stress would be required to maintain plastic deformation via dislocation movement. Typical values for k and σ_0 are $k \approx 0.5$ MN/m^{3/2} and $\sigma_0 \approx 50$ MPa, respectively, for a hexagonal close-packed metal.¹¹ Assuming a crystal

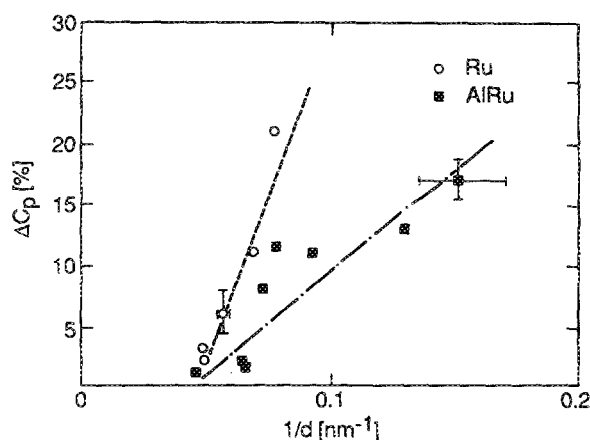


FIG. 9. Increase of the specific heat for Ru and AlRu as a function of reciprocal crystal size.

size of 10 nm, the minimum-yield stress is of the order of 5 GPa. On the hand, the maximum theoretical shear stress of Ru is approximately 32 GPa. Thus, the small crystal size itself provides a limit for the glide of dislocations and therefore for further crystal size refinement, since the forces required cannot be provided by ball milling. In contrast, plastic deformation of nanocrystalline material seems to occur at considerably lower stresses via a gliding along the grain boundaries as has recently been shown for nanocrystalline ceramics.¹²

Disordering in AlRu is monitored by the change in long-range order as is shown in Fig. 5. In comparison to the experimentally observed change of the long-range-order parameter S/S_0 , the influence of the grain boundaries has been estimated by assuming that one monolayer on the surface of each crystal sees no long-range order. AlRu before ball milling was used as reference, assuming perfect-order $S/S_0 = 1$. As expected, the long-range order decreases linearly with $1/d$ (dotted line). The experimentally observed decrease is slightly larger and cannot be explained only by the grain-boundary contribution. The deviation has its maximum at the same crystal size where the strain reaches its maximum value. Thus, ball milling seems to disorder AlRu by both crystal refinement and lattice disorder. Disordering is likely to occur by a high dislocation density, which in turn implies a high density of antiphase boundaries. However, one can estimate from the difference between the two curves that only approximately 5% of the Al or Ru atoms occupies the wrong lattice sites due to the strain, i.e., antiphase boundaries or Fe impurities. Crystal refinement is the prevalent disordering mechanism. Since the decrease in crystal size is very slow, it appears that S/S_0 approaches a finite value after long ball milling.

Crystal refinement leads to an increase in the number of grain boundaries, and therefore many atoms are located in interfacial areas. Changes in physical properties when the crystal size reaches a nanometer scale have been observed by Birringer *et al.*,¹³ who prepared nanocrystalline materials by an inert-gas condensation technique. They claim that the interfacial component exhibits a gaslike atomic arrangement without short- or long-range order, which is responsible for the differences in physical properties. In particular, the continuous increase in specific heat as the crystal dimension approaches a nanocrystalline scale indicates the destabilizing influence of this interfacial component. It can be associated with an increase in the configurational and vibrational entropy due to interfacial disorder and lattice defects, i.e., dislocations, grain boundaries, vacancies, and impurities. The reduction of Δc_p by approximately 12% after an annealing treatment at high temperature shows that grain boundaries and lattice defects are mainly responsible for the increase in specific heat. Similar enhancements of 10%–40% have been observed in nanocrystalline Cu and Pd,¹⁴ respectively. Moreover, investigations on thermal expansion of grain boundaries in copper polycrystals show that the thermal-expansion coefficient of a grain boundary is about 2.5–5 times larger than in the bulk material owing to large anharmonic vibrations.¹⁵ A change in thermal expansion would also lead to an increase in c_p . It was not possible to get back

to the initial specific-heat value after annealing. The iron impurities after long ball milling may provide an explanation: The Ru-Fe solid solution probably has a lower Debye temperature than pure Ru with about 500 K. This in turn would result in an increase of the heat capacity.

Ball milling also enhances the lattice strain considerably. Strain of 1% for pure elements and 3% for intermetallic phases are characteristic for heavily deformed metals.¹ The main contribution to lattice strain in ball-milled samples is probably the dislocation density. Obviously the dislocation density increases rapidly in the beginning of the deformation process and reaches a maximum or even decreases when the crystal size gets very small. This can be understood as due to the above-mentioned change in deformation mechanism. A saturation of the dislocation density is expected, if with small grain size plastic deformation no longer occurs by formation and glide of dislocations, but by a glide along the grain boundaries as already discussed. The large reduction in strain for AlRu can perhaps be attributed to the smaller crystal sizes. An open question remains as to the minimum crystal size for which dislocations are stable, but it has been shown that free surfaces act as a sink for dislocations and reduce the dislocation density in the bulk considerably.¹⁶ In addition lattice strain may also arise from the increasing grain boundary contribution and from the Fe impurities. Although the volume mismatch between Fe and Ru atoms is small and Fe and Ru form an extended solid solution in the equilibrium-phase diagram, the impurities will nevertheless produce some lattice strain. Since the strain increases rapidly in the beginning of the deformation process, when the Fe content is still small, this contribution is likely to be small. The experimentally observed saturation and subsequent decrease of the rms strain as a function of decreasing particle size is a hint that the dislocation density and not impurities or grain boundaries are dominating.

Although most of the mechanical energy expended in the ball-milling process is converted into heat, a part is stored in the metal and released during recovery and recrystallization. The observed heat release of 6 kJ/mol for AlRu and 10 kJ/mol for Ru exceeds by far the energies stored by conventional techniques as cold rolling or wire drawing.¹ For Ru, the stored heat is close to 40% of the heat of fusion of the pure element. The decrease of the enthalpy after long ball milling may be attributed to the decreasing strain and to the increasing impurity content. It is known that impurities lead to an increase of the recrystallization and recovery temperature. Since the temperature range of the DSC4 is limited to 870 K, this would in turn result in an apparent decrease of the heat release. It is not yet understood whether the heat is stored mainly by the grain boundaries or by the lattice strain. The strain energy W_s depends on the rms strain as $W_s = \langle \epsilon^2 \rangle / 2Y$, where Y is Young's modulus. In Fig. 10 the heat release is plotted as a function of $\langle \epsilon^2 \rangle$. The roughly linear dependence for Ru indicates that energy storage is mainly due to strain. For AlRu, a systematic strain dependence is not obvious. Since the crystal size is much smaller after ball milling, we conjecture that energy is predominantly stored in grain boundaries.

One might speculate why Ru and AlRu do not trans-

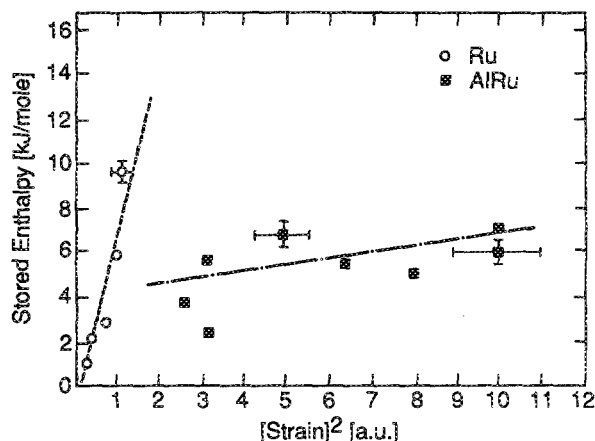


FIG. 10. Heat release for Ru and AlRu as a function of (strain).

form into an amorphous structure after ball milling as has previously been demonstrated to be possible for several intermetallic compounds (for a recent review see Ref. 17). A necessary condition for amorphization is that the free energy of the crystalline phase is raised above the free energy of the amorphous phase. The free-energy change ΔG after ball milling is given by $\Delta G = \Delta H - T \Delta S$, where ΔH and ΔS are the respective changes in enthalpy and entropy. For Ru and AlRu, the stored enthalpy can be directly measured and is of the same order as typical crystallization enthalpies of binary amorphous alloys. However, larger difficulties arise if one wants to estimate the change in entropy. Deformation results in a change of the configurational and vibrational contribution of the entropy. To determine the total difference in entropy versus temperature and to separate the two contributions, detailed low-temperature specific-heat measurements would be necessary in addition to the existing specific-heat data at higher temperature. However, the large increase in specific heat implies that these changes are considerable. They might lead to a drastical elastic softening and to a crystal-to-glass transition with further crystal refinement. Obviously, effective reordering mechanisms in AlRu and Ru are the main reason why amorphization was not possible. This view is supported by the fact that it was impossible to reduce the long-range-order parameter S in AlRu to less than 0.7 even after long ball milling.

V. SUMMARY

We have shown that ball milling of Ru and AlRu produces a mixture of high-angle grain boundaries and highly strained crystal lattices on a nanometer scale. The crystal size decreases, but appears to saturate at less than 12 nm for Ru and 7 nm for AlRu after long processing times. At the same time, the lattice strain is enhanced up to 1% for Ru and 3% for AlRu. Both mechanisms disorder the crystal as is

shown by the decreasing long-range-order parameter in AlRu.

In addition, the heat capacity and the stored energy of cold work have been measured by means of differential scanning calorimetry. The specific heat increases by almost 15% for AlRu and 20% for Ru. This indicates changes in the vibrational and configurational part of the entropy, probably due in part to large anharmonic atomic vibrations at grain boundaries and disordered lattice sites. The stored energy of cold work is almost 6 kJ/mol for AlRu and 10 kJ/mol for Ru, exceeding by far known values for conventional deformation techniques. Further information about the mechanisms which destabilize crystal lattices in the ball-milling process could be gained by low-temperature specific-heat experiments. In addition, we suggest studies of the longitudinal and shear sound velocity to get information on the change of the elastic constants.

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